Low-Temperature Emission Control to Enable Fuel-Efficient Engine Commercialization

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Oak Ridge National Laboratory

National Transportation Research Center

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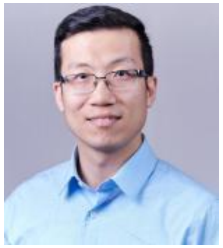
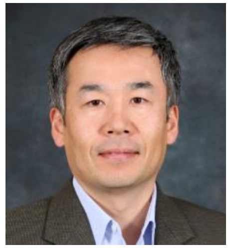
Acknowledgements

- ORNL Low Temperature Catalysis Team
  - Andrew Binder,† Shuai Tan,‡ Jae-Soon Choi, Jim Parks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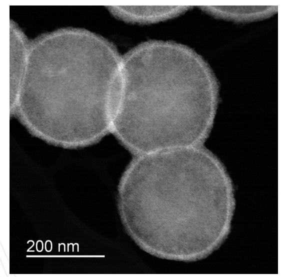
- DOE funding
  - Advanced Combustion Systems
  - Ken Howden, Gurpreet Singh, and Michael Weismiller

U.S. Department of Energy | Energy Efficiency & Renewable Energy

VEHICLE TECHNOLOGIES OFFICE

- Access to instrumentation
  - Micrographs and elemental maps captured using instrumentation (FEI Talos F200X S/TEM) provided by the Department of Energy, Office of Nuclear Energy, Fuel Cycle R&D Program and the Nuclear Science User Facilities



† - Andrew Binder is now a Chromatography Chemist at Galbraith Laboratories, Inc. in Knoxville, TN

‡ - Shuai Tan is now an R&D Engineer at UOP-Honeywell in Chicago, IL

Project Overview

Timeline

- Year 3 of 3-year program*

Budget

- FY2017: $400k (Task 1*)
- FY2018: $300k (Task 1*)

*Task 1: Low Temperature Emission Control

Part of large ORNL project “Enabling Fuel Efficient Engines by Controlling Emissions” (2015 VTO AOP Lab Call)

Partners

- Low Temperature Aftertreatment Sub-Team of US DRIVE Advanced Combustion and Emission Control Tech Team
- Johnson Matthey
- Solvay
- NSF-funded scientists/students from University of South Carolina
- University at Buffalo (SUNY)

Barriers

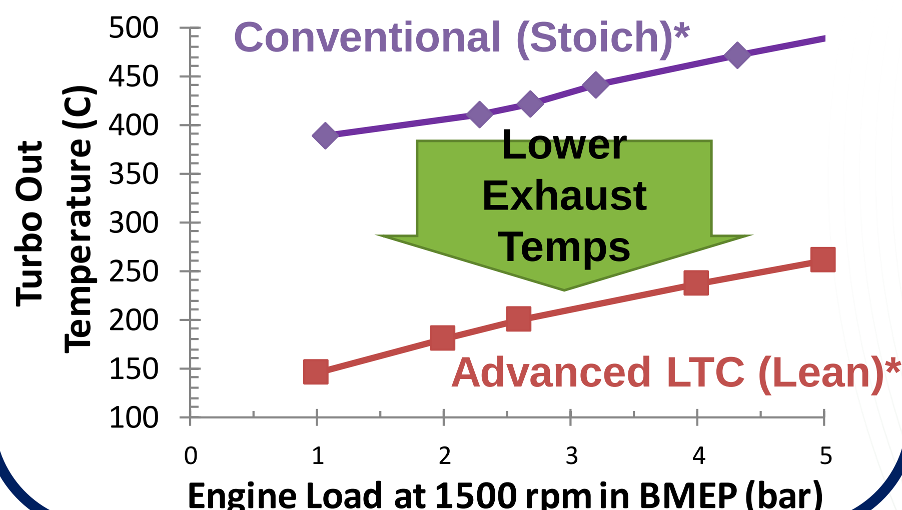
- Addressing emission compliance barrier to market for advanced fuel-efficient engine technologies, such as **90% conversion of NOx, CO and HC at 150°C**

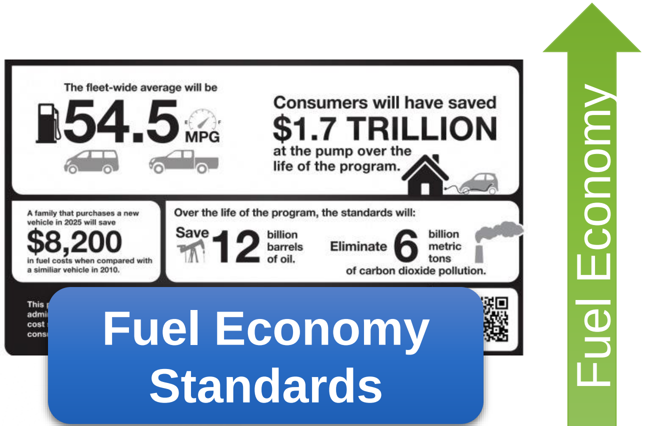
Objectives and Relevance

Develop new emission control technologies to enable fuel-efficient engines with low exhaust temperatures (<150°C) to meet emission regulations
Goal: 90% Conversion at 150°C

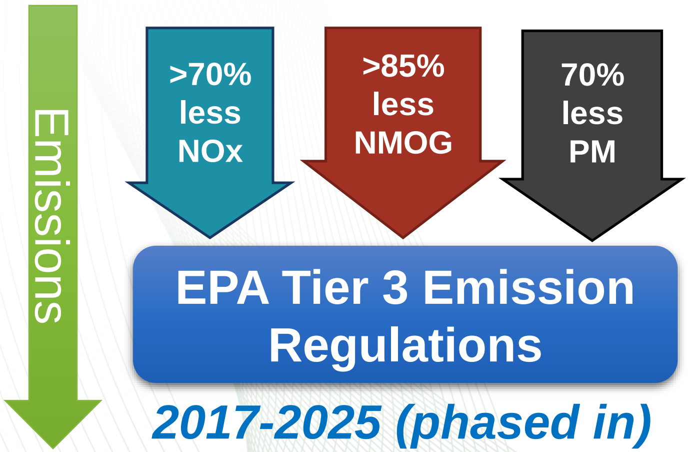
- Greater efficiency lowers exhaust temperature
- Catalysis is challenging at low temperatures
- Emissions standards getting more stringent

Higher efficiency engines have lower exhaust temperatures





54.5 mpg CAFE by 2025



2017-2025 (phased in)

* "**Conventional**": modern state-of-the-art GDI Turbocharged (stoichiometric)
* "**Advanced LTC**": advanced lean-burn Low Temperature Combustion (LTC) engine

Relevance: Guiding Documents Define Needs

2015 CLEERS Industry Priorities Survey

USDRIVE "The 150°C Challenge" Workshop Report

USDRIVE ACEC Tech Team Roadmap (2013)

Identified Needs Addressed:

- Lower temperature CO and HC oxidation
- Low temperature NOx reduction
- Cold start emission trapping technologies
  - Especially passive NOx adsorbers
- Reduced PGM
- Better durability
- Promote innovative catalytic solutions via partnering with DOE BES programs

Relevant to all combustion approaches cited in ACEC Tech Team Roadmap

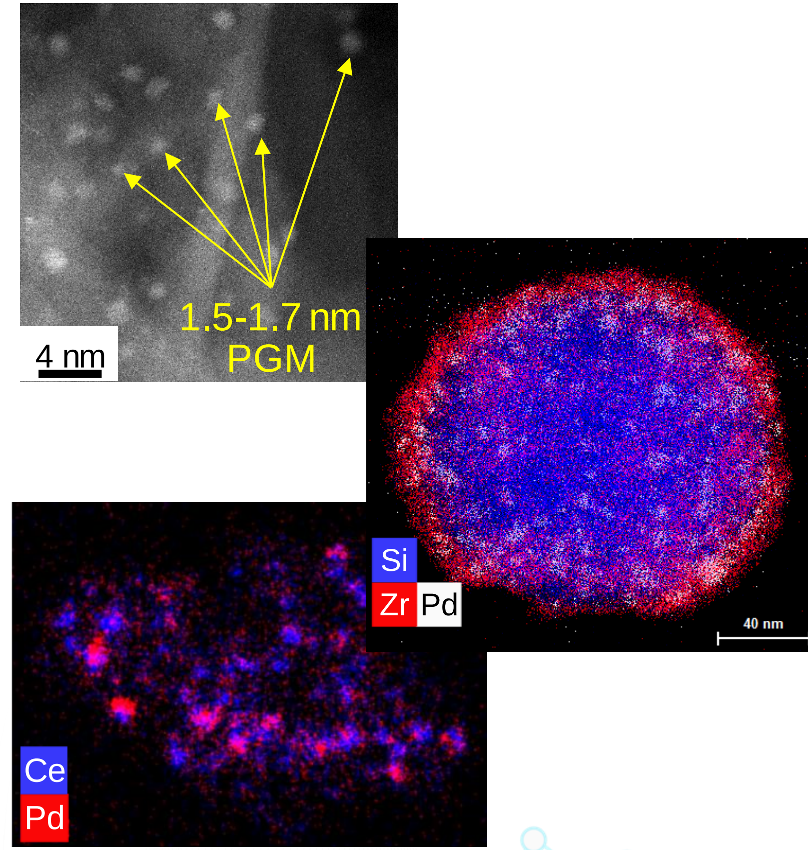
Low Temperature Combustion (LTC)

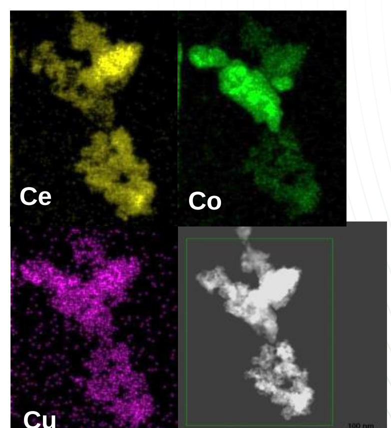
Dilute Gasoline Combustion

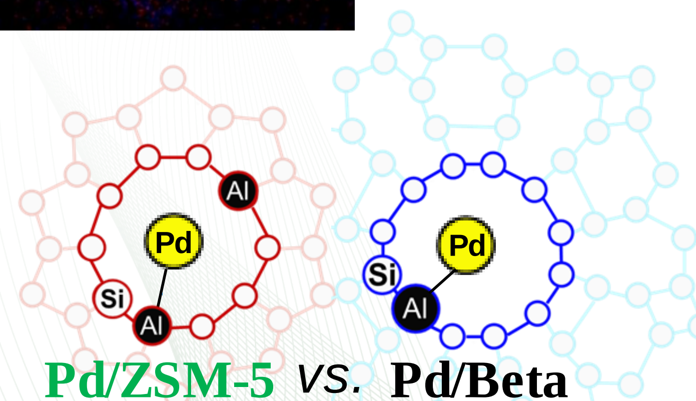
Clean Diesel Combustion (CDC)

Approach

- Advanced concepts through collaborations
  - Universities and BES-funded scientists
  - Evaluate promising materials w/ ACEC protocols
- Enhance conventional catalysts through support modifications
  - Maximize PGM utilization with improved durability
  - Core@shell approaches with metal oxides
  - Targeted deposition of PGM on nanoparticles of Ce- and Ce-Zr supported on alumina
- Passive adsorber/trap materials
  - Hold onto emissions until catalysts are active
  - Passive NOx adsorbers
  - Hydrocarbon traps
- Novel materials (high risk)
  - PGM free metal oxides







Collaborations

- **DOE Basic Energy Science researchers**
  - Sheng Dai and Ashi Savara (ORNL), Center for Nanophase Materials Science (ORNL)
- **CLEERS**
  - Dissemination of data; presentation at CLEERS workshop
- **Academia**
  - **University of South Carolina:** Professors John Regalbuto, Jochen Lauterbach, Erdem Sasmaz
  - **University at Buffalo (SUNY):** Professor Eleni Kyriakidou
  - **University of Tennessee:** Professors Siris Laursen and Sheng Dai
- **Industry**
  - **USCAR/USDRIVE Low Temperature Aftertreatment (LTAT) working group**
    - low temperature evaluation protocols
  - **Catalyst and washcoat suppliers**
    - **Johnson Matthey:** Industry input from Haiying Chen, washcoating collaboration
    - **Solvay:** alumina-based supports provided for PGM support studies at USC (Barry Southward)
    - Presentations given at **Umicore, BASF, Hee-Sung, Hyundai, Ford**
- **Other DOE-funded FOA Projects**
  - **Ford**-led project: Next Generation Three-Way Catalysts for Future, Highly Efficient Gasoline Engines
    - Catalysts being investigated for stoichiometric applications
  - **UCONN**-led project: Metal Oxide Nano-Array Catalysts for Low Temperature Diesel Oxidation

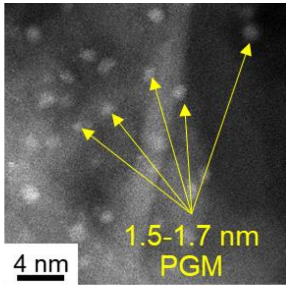
Milestones

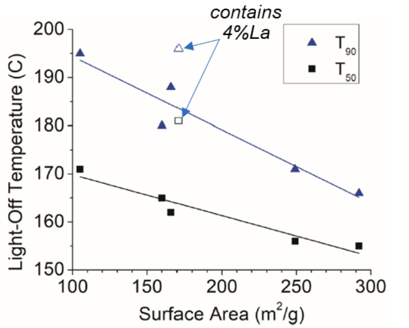
- **FY17 Milestones:** ***complete***
  - Develop capability to washcoat novel powder catalysts (9/30/2017).
    - Achieved on cores and full-size monolith

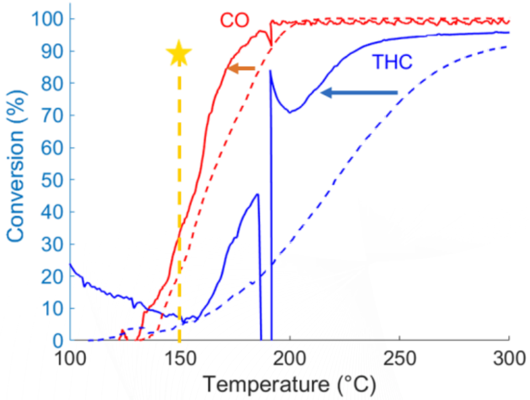
- **FY18 Milestones** ***on track***
  - Achieve 90% conversion of CO, HC, and NOx with catalytic emission control in a flow reactor

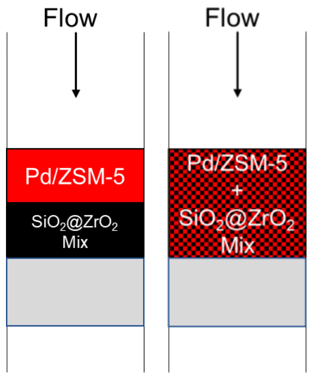
Summary of Technical Accomplishments

- ORNL/USC/Solvay Collaboration PGM/advanced supports
  - Showed that 10-30% SiO_2 content in Al_2O_3 improves reactivity
  - Andrew Wong received PhD from U-So.Car.*
- Trapping materials
  - Employed USDRIVE protocol for trapping
  - Demonstrated trap materials function effectively as oxidation catalysts
  - Verified aging degrades overall trap functionality, but $C_{10}H_{22}$ still trapped efficiently
- Multifunctional evaluation
  - Demonstrated mixed bed configurations have markedly better performance vs. dual bed
- Washcoating advances
  - Full-size washcoated monolith of CCC+Pt/Al_2O_3
  - In collaboration with JMI, washcoated Pd/Ce-Zr_{NP}/Al_2O_3 and Pt/Ce-Zr_{NP}/Al_2O_3 samples









‡ - Andrew Wong has accepted a position at UOP-Honeywell

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Employ low temperature protocols to evaluate novel catalysts

- Project uses US DRIVE Advanced Combustion and Emission Control Team Aftertreatment Protocols for Catalyst Characterization and Performance Evaluation

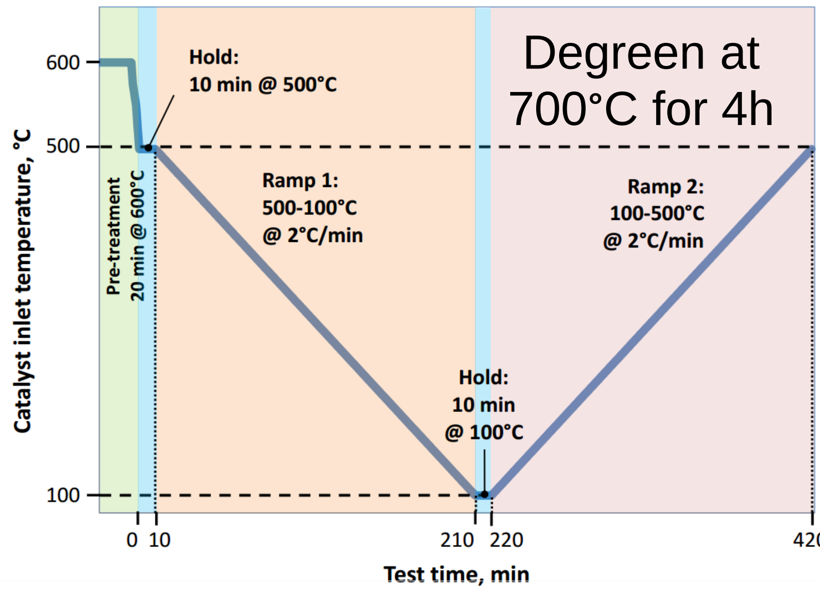
- Full protocol at: www.CLEERS.org

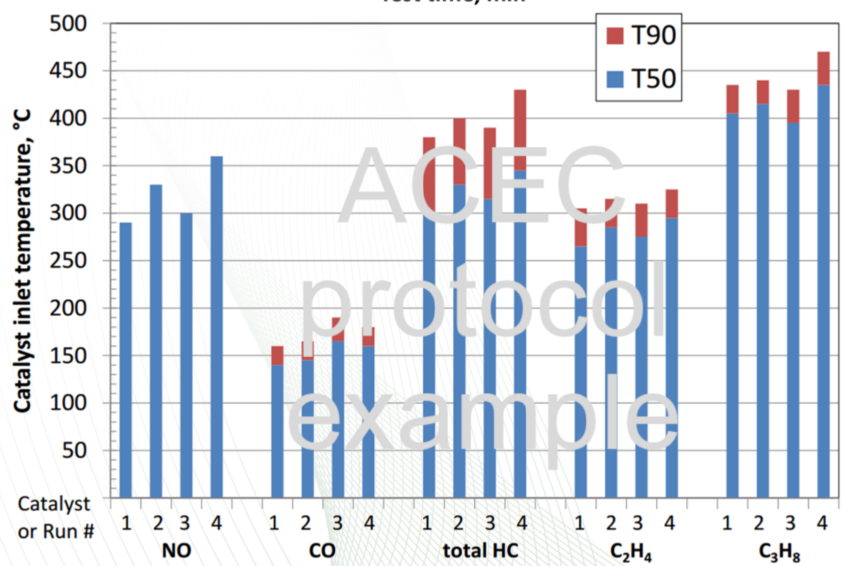
LTC-D: Low Temp. Combustion Diesel

Total HC_1:	3000 ppm
C_2H_4:	500 ppm
C_3H_6:	300 ppm
C_3H_8:	100 ppm
*$C_{12}H_{26}$:	2100 ppm
CO:	2000 ppm
NO:	100 ppm
H_2:	400 ppm
H_2O:	6 %
CO_2:	6 %
O_2:	12 %
Balance N_2	

Powder Catalyst Requirements

- Reactor ID 3-13 mm
- Catalyst particle size ≤ 0.25 mm (60 mesh)
- Catalyst bed L/D ≥ 1
- Space velocity
  - 200-400 L/g-hr
  - For 0.1 g, flow 333-666 sccm





* - we employed decane ($C_{10}H_{22}$) due to bubbler needs

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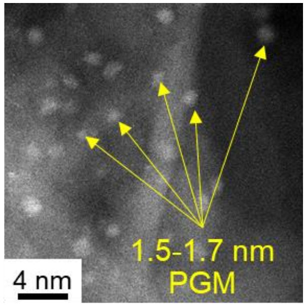
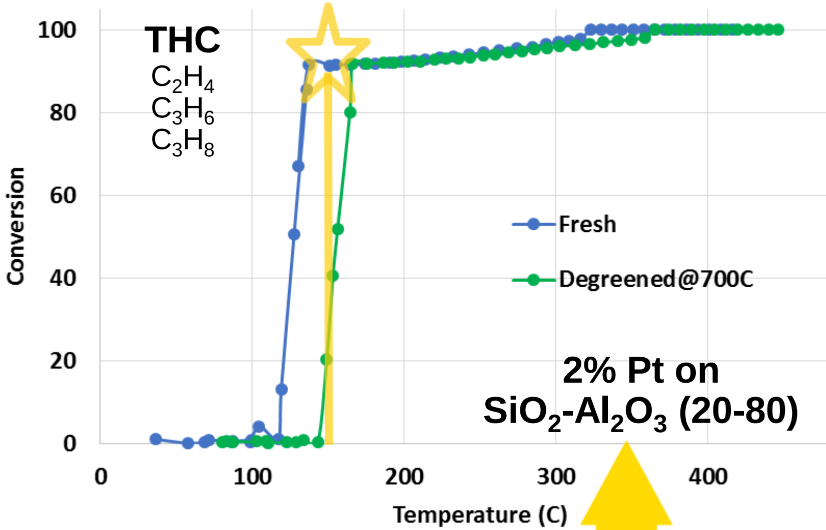
University of South Carolina (USC) and Solvay collaboration yielding promising results for PGM catalysts

- University of South Carolina (USC) and Solvay collaboration
  - Prof. Regalbuto (USC) has been leading research on Strong Electrostatic Adsorption (SEA) of PGM on standard supports
    - Superb initial PGM dispersion
  - Solvay collaboration started
    - A leader in stable supports
    - Provided 7 supports
      - 70-100% Al, 0-30% Si, 0-4% La
- USC synthesis of Pt:Pd DOCs
  - Target PGM total: 2 wt%
  - Pt:Pd - 1:0, 3:1, 1:1, 1:3, 0:1
- Research objectives
  - Does stable commercial support lead to enhanced durability?
  - Are Pt/Pd bimetallics more stable?

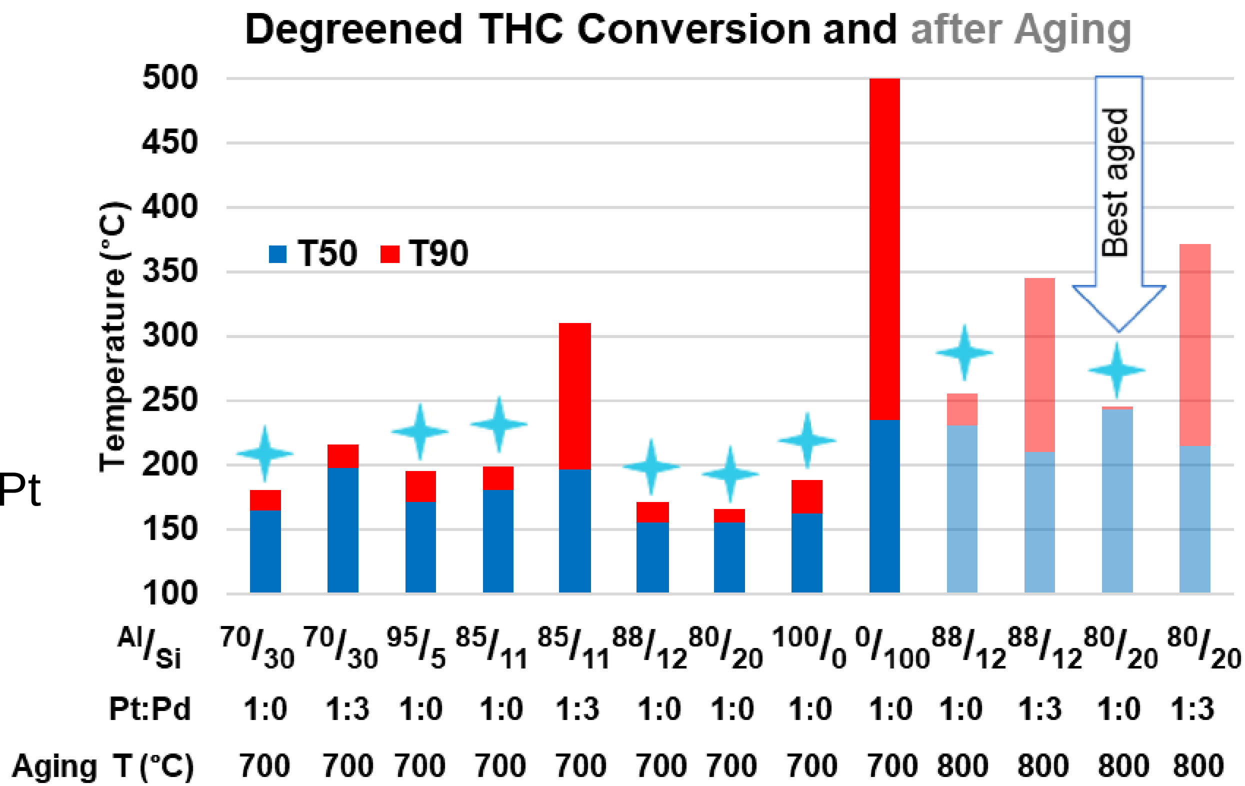


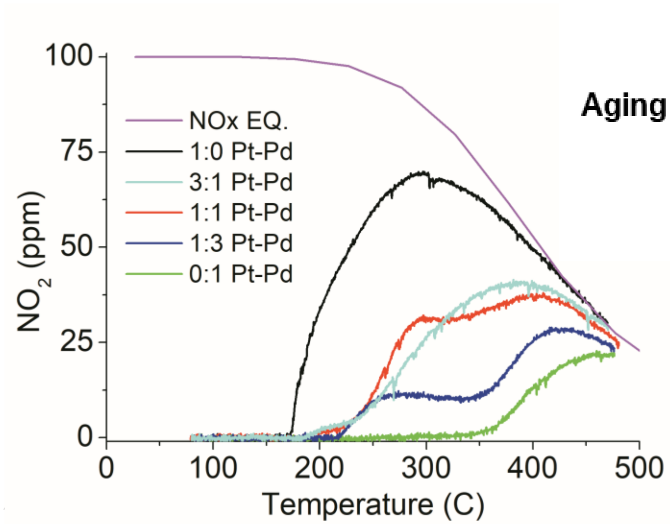


Al_2O_3 (wt%)	SiO_2 (wt%)	Surf. Area (m^2/g)
100	0	160
95	5	105
85	11 + 4% La_2O_3	171
88	12	249
80	20	292
70	30	160
0	100	282

Pt-only (✦) catalysts continue to show lowest T_{90} for degreened and aged catalysts regardless of support

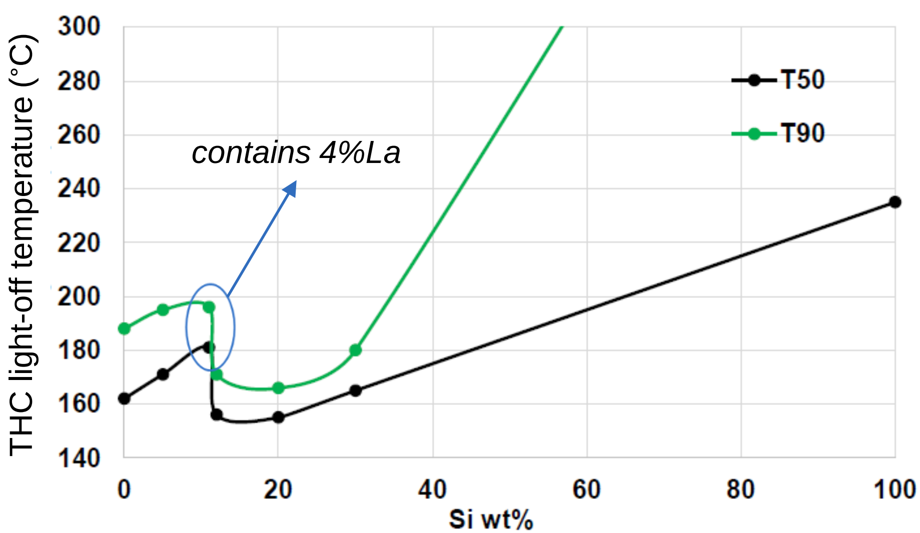
- Expected improvement from Pd/Pt bimetallic depositions not realized with activity
  - improved durability seen with T_{50}, but not T_{90}
- Additional benefit of high NO to NO_2 oxidation for particulate oxidation with Pt

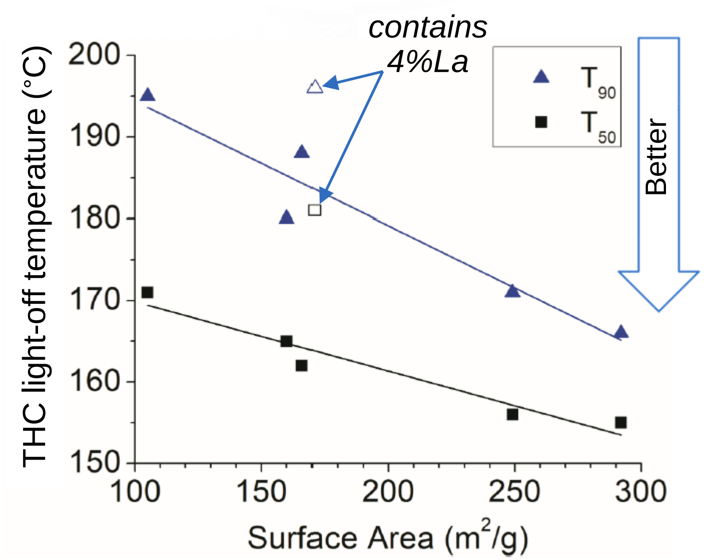




Support variation study indicates 10-30% SiO_2, high surface area, and 0% La benefit THC reactivity

- Observations noted for Pt-only catalyst samples for THC light-off temperatures
- Notable decrease in both T_{50} and T_{90} observed for non-La containing supports when increasing from 5% SiO_2 to 10-30% SiO_2
- Although not surprising, distinct trend in surface area is observed
  – Only exception is the La containing support, which is notably less active



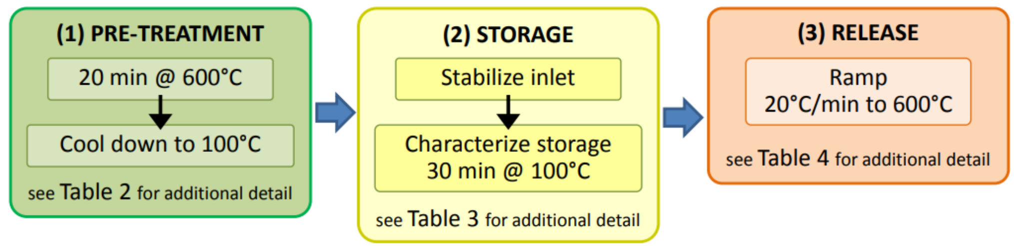


Studies of HC/NOx Traps use USDRIVE Trapping Protocol

- Protocol finalized in March 2018 by the Low Temperature Aftertreatment Sub-Team of the US DRIVE Advanced Combustion and Emission Control Team (www.CLEERS.org)

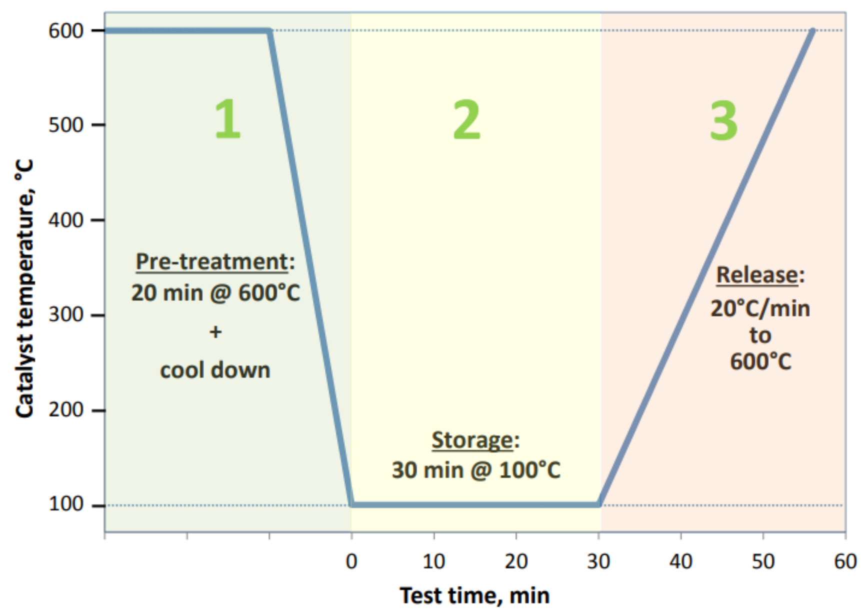
- Key features:
  - Long initial storage treatment
  - Rapid heating rate of 20°C/min
  - Aromatic and heavy HCs dominate speciation
  - Ethanol included in gasoline-relevant conditions

Degreen at 700°C for 4h



LTC-D: Low Temp. Combustion Diesel

Total HC_1:	3000 ppm	NO:	100 ppm
C_2H_4:	900 ppm	H_2:	400 ppm
C_7H_8:	900 ppm	H_2O:	6 %
$C_{12}H_{26}$:	1200 ppm*	CO_2:	6 %
CO:	2000 ppm	O_2:	12 %
		Balance N_2	

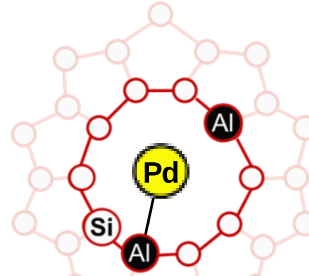


Also need to be able to survive 800°C for 50 h and be tolerant of sulfur (5 ppm SO_2 for 5h at 300°C)

* - we employed decane ($C_{10}H_{22}$) due to bubbler needs

Pd/ZSM-5 captures high percentage of HCs and NO in first three minutes of protocol; release varies with species

- Pd/ZSM-5 stores a considerable amount of NO, toluene (C_7H_8) and decane ($C_{10}H_{22}$) with a peak release centered around 210 °C
  - HC release initiates immediately upon heating

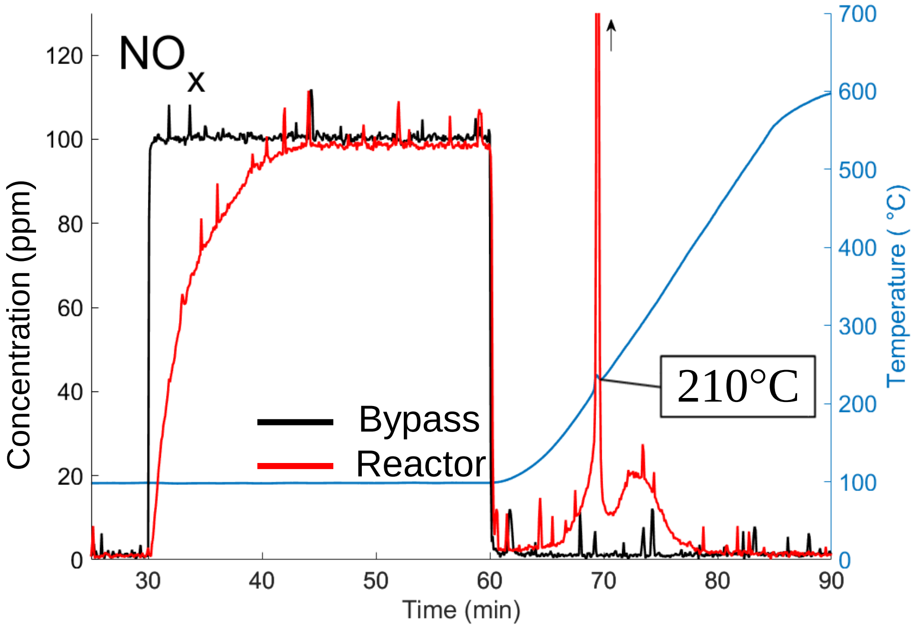


Pd/ZSM-5

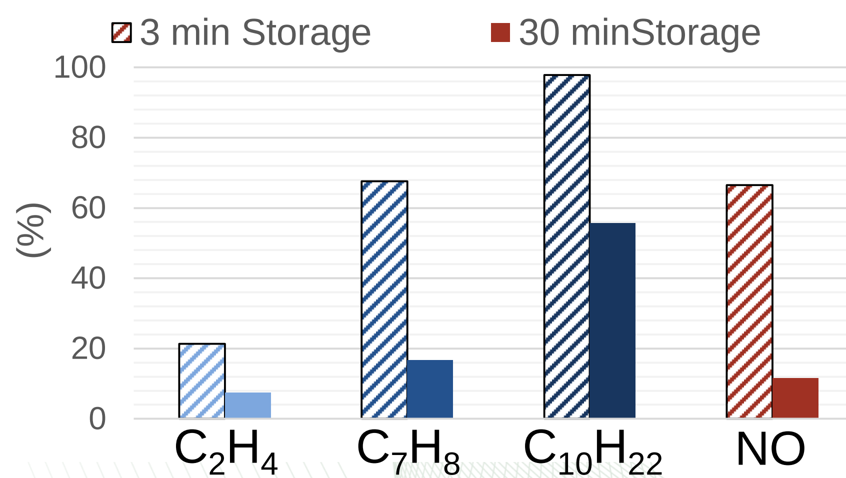
Zeolite type	Si/Al molar ratio	Nominal cation form	Surface area (m^2/g)
ZSM-5	15	1% Pd^{2+}	~400

Initial calcination: 500 °C (2 h)
Degreened at 700 °C (4 h)

Pd/ZSM-5 Storage and Ramp



	C_2H_4	C_7H_8	$C_{10}H_{12}$	NO
Total Stored (mg/g_{cat})	2.11	4.43	21.32	0.78
3 min storage (mg/g_{cat})	0.52	0.95	2.04	0.45



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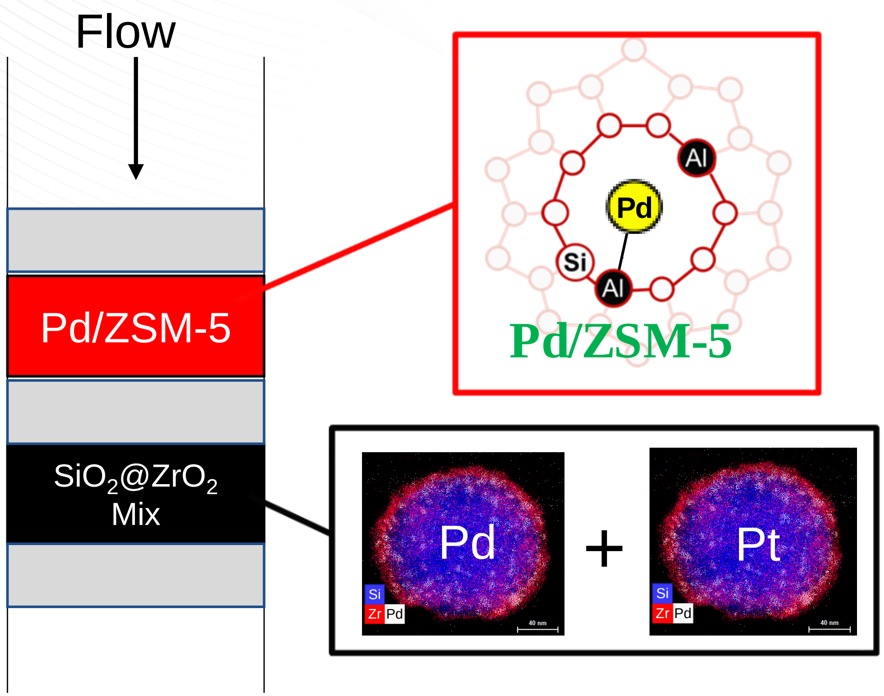
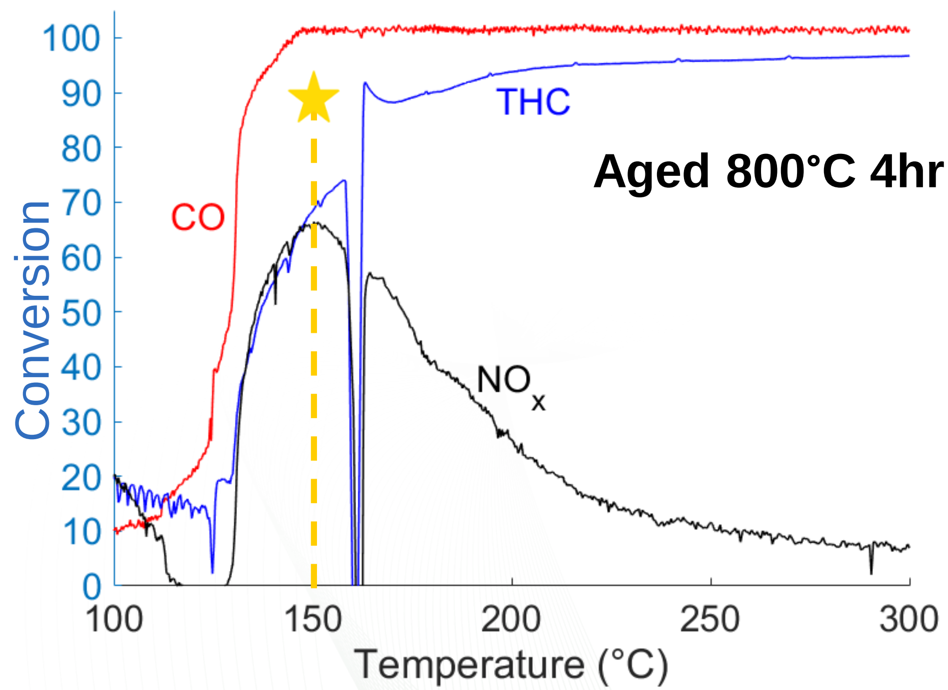
A dual-bed approach with a trap in front of the oxidation catalyst has been shown to be a promising approach

Combining Pd/ZSM-5 trapping material with most active oxidation catalyst (OC) shows significant improvement under lightly aged conditions





- Catalyst system reaches a **T_{90} = 134ºC** for **CO** and **177ºC** for **HC**
- Significant release of hydrocarbons and NO_x occurs at 162ºC
- Additional aging necessary on each component

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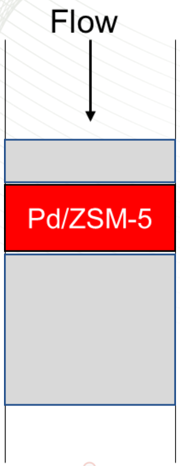
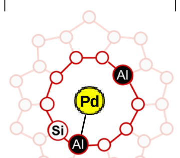
Individual components studied with modified trapping protocol to understand specific role and impact of aging

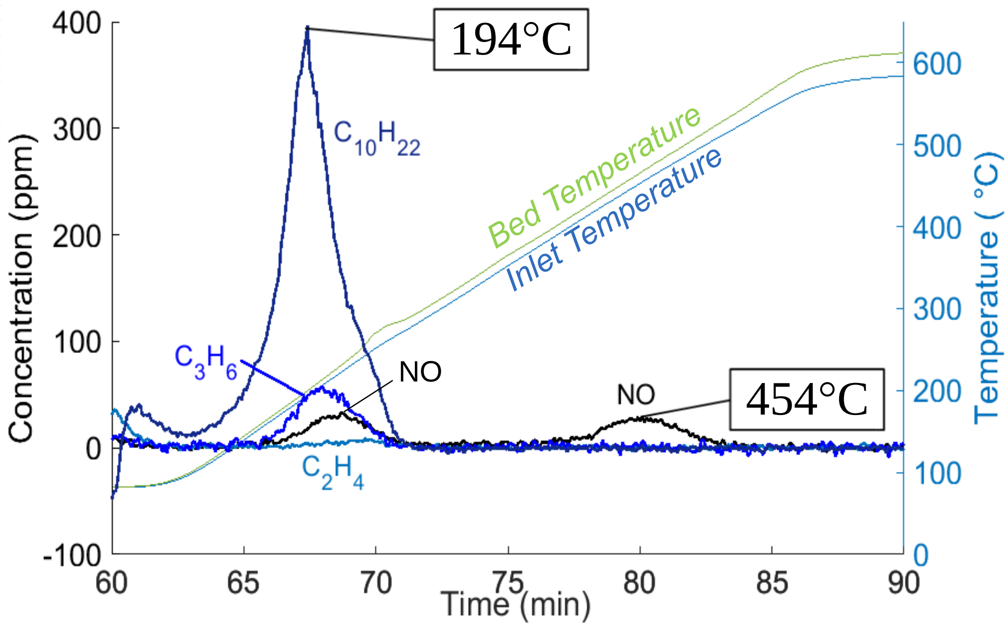
HC composition changed to reflect oxidation protocol

Initial Pd/ZSM-5 only: HC/NO release following 30 min storage





Pd/ZSM-5



	Release Temp	Release %
NO_x	222ºC / 454ºC	94%
C_2H_4	242ºC	9%
C_3H_6	205ºC	59%
$C_{10}H_{22}$	194ºC	48%

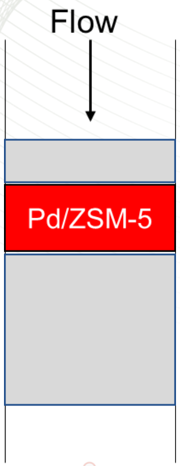
Conditions during 30 min storage step at 100°C

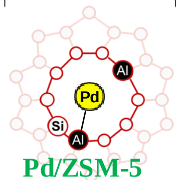
total HC_1: 3000 ppm
C_2H_4: 500 ppm
C_3H_6: 300 ppm
C_3H_8: 100 ppm
$C_{10}H_{22}$: 2100 ppm
CO: 2000 ppm
NO: 100 ppm
Also H_2, O_2, H_2O and CO_2

- Pd/ZSM-5 shows favorable release temperatures for pairing with an active DOC catalyst
- Nearly 100% release of NO across two peak temperatures
- Significant oxidation catalyst-type reactivity observed due to presence of Pd

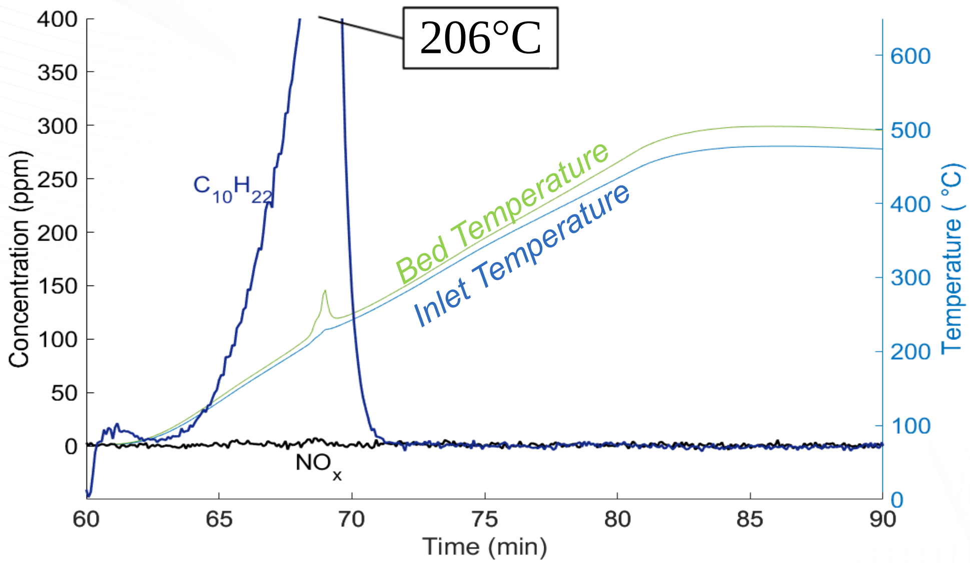
Aged Pd/ZSM-5 only traps decane, $C_{10}H_{22}$, effectively; however, oxidation functionality diminished

Protocol aging: reaction conditions at 800°C for 50h, 5 ppm SO_2 @ 300ºC 5 h





AGED Pd/ZSM-5 only: HC/NO release following 30 min storage



	Release Temp	Release %
NO_x	N/A	N/A
C_2H_4	N/A	N/A
C_3H_6	N/A	N/A
$C_{10}H_{22}$	230ºC	94%

Conditions during 30 min storage step at 100°C

total HC_1: 3000 ppm
C_2H_4: 500 ppm
C_3H_6: 300 ppm
C_3H_8: 100 ppm
$C_{10}H_{22}$: 2100 ppm
CO: 2000 ppm
NO: 100 ppm
Also H_2, O_2, H_2O and CO_2

- Most functionality of Pd/ZSM-5 lost after aging; however, decane is still trapped very effectively
  - decane release temperature also increases
- Minimal C_2H_4, C_3H_6, C_3H_8, NO_x stored/released
- Aging nearly eliminates the oxidation catalyst-type reactivity observed (release = storage)

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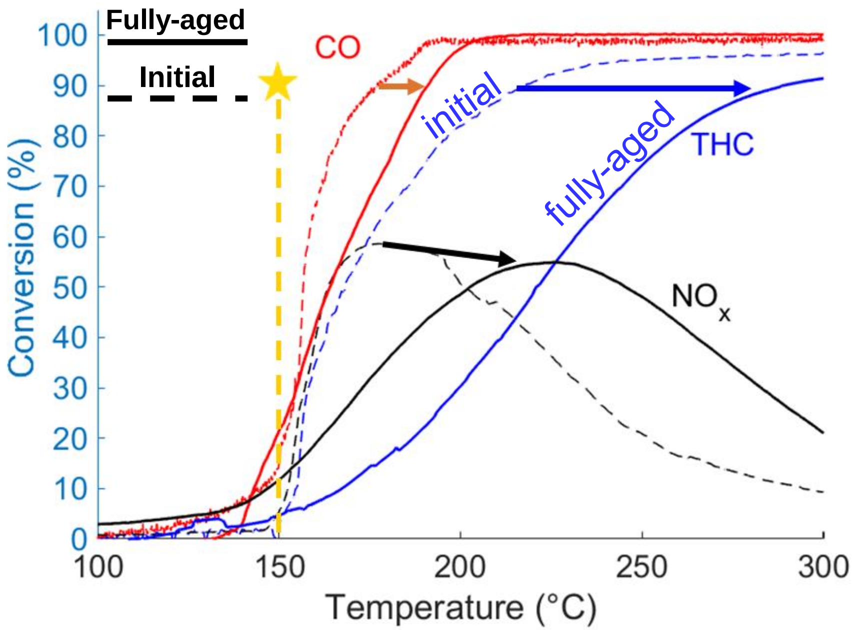
Oxidation catalyst mixture reactivity diminishes after additional hydrothermal aging and sulfation

Protocol aging: reaction conditions at 800°C for 50h, 5 ppm SO_2 @ 300ºC 5 h

AGED Pd+Pt Oxidation Catalysts: lightoff temperatures increase 15-70ºC



T_{90} (ºC)	800ºC 4h	800ºC 50h + sulfation
CO	177	191
THC	206	279
C_2H_4	178	243
C_3H_6	206	272
C_3H_8	383	508
$C_{10}H_{22}$	203	267

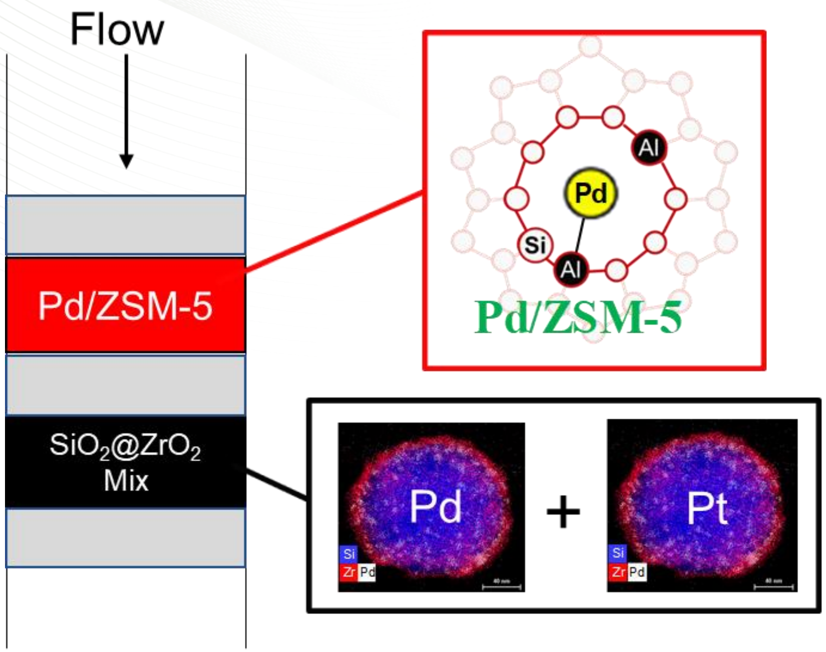
Conditions during 2ºC ramp

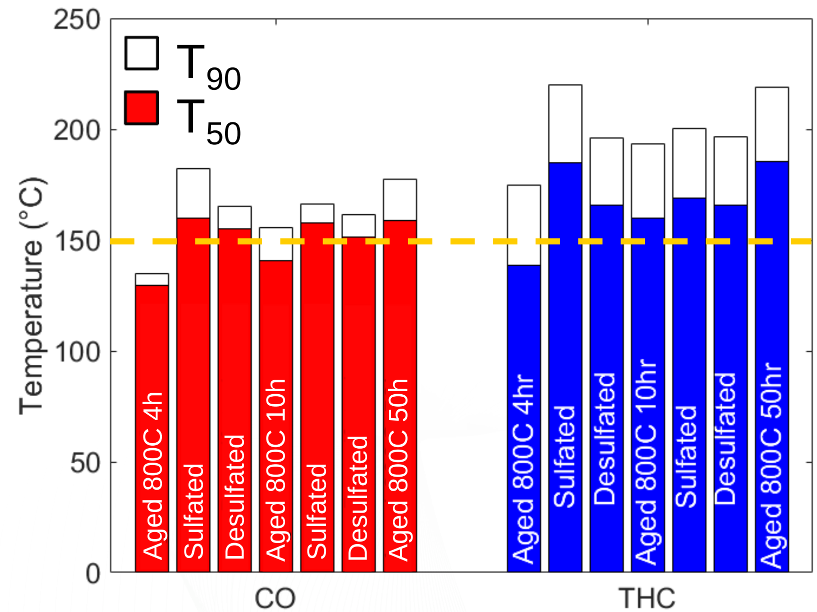
total HC_1: 3000 ppm
C_2H_4: 500 ppm
C_3H_6: 300 ppm
C_3H_8: 100 ppm
$C_{10}H_{22}$: 2100 ppm
CO: 2000 ppm
NO: 100 ppm
Also H_2, O_2, H_2O and CO_2

- CO light-off only show moderate 14ºC increase in T_{90}
- All HCs show lost low temperature activity
  - C_2H_4, C_3H_6, and $C_{10}H_{22}$ increase 63-66ºC, C_3H_8 increases 125ºC
- Notably, NO oxidation to NO_2 increases in reactivity on the aged samples above 200ºC

Aging in the full dual-bed configuration significantly lessens deactivation

Protocol aging: reaction conditions at 800°C for 50h, 5 ppm SO_2 @ 300ºC 5 h
Desulfation under cycling lean-rich conditions for 30 min at 500ºC, 30s per condition





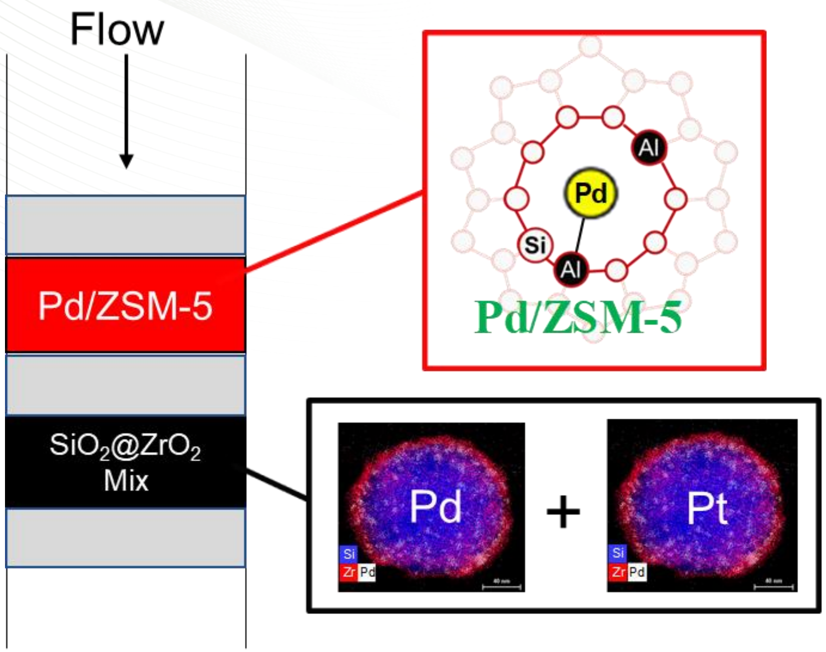
Conditions during 2ºC ramp

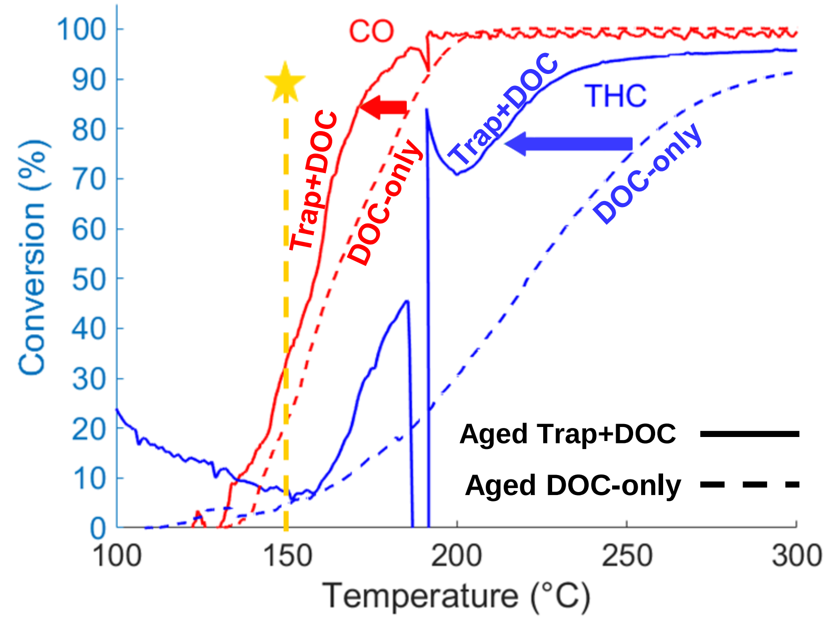
total HC_1: 3000 ppm
C_2H_4: 500 ppm
C_3H_6: 300 ppm
C_3H_8: 100 ppm
$C_{10}H_{22}$: 2100 ppm
CO: 2000 ppm
NO: 100 ppm
Also H_2, O_2, H_2O and CO_2

- After full aging and sulfation protocol CO and THC light-off temperatures only increase ~40 ºC:
  - CO: T_{90} = 134 to 177 ºC
  - HC: T_{90} = 177 to 218 ºC

Aging in the full dual-bed configuration significantly lessens deactivation

Protocol aging: reaction conditions at 800°C for 50h, 5 ppm SO_2 @ 300ºC 5 h
Desulfation under cycling lean-rich conditions for 30 min at 500ºC, 30s per condition





Conditions during 2ºC ramp

total HC_1: 3000 ppm
C_2H_4: 500 ppm
C_3H_6: 300 ppm
C_3H_8: 100 ppm
$C_{10}H_{22}$: 2100 ppm
CO: 2000 ppm
NO: 100 ppm
Also H_2, O_2, H_2O and CO_2

- After full aging and sulfation protocol CO and THC light-off temperatures only increase ~40 ºC:
  - CO: T_{90} = 134 to 177 ºC
  - HC: T_{90} = 177 to 218 ºC
- Although Pd/ZSM-5 trap is heavily degraded, it still improves reactivity of system considerably in dual-bed configuration

Fast ramp (40°C/min) employed to evaluate HC/NO trap as an oxidation catalyst

- Straightforward evaluation is difficult due to storage properties of Pd/ZSM-5
- Ramping at 40°C/min allows a pseudo cold-start evaluation
  - Reactant gas stream established in bypass
  - Introduce to reactor w/ immediate ramp
- Significant storage initially observed, followed by release and conversion

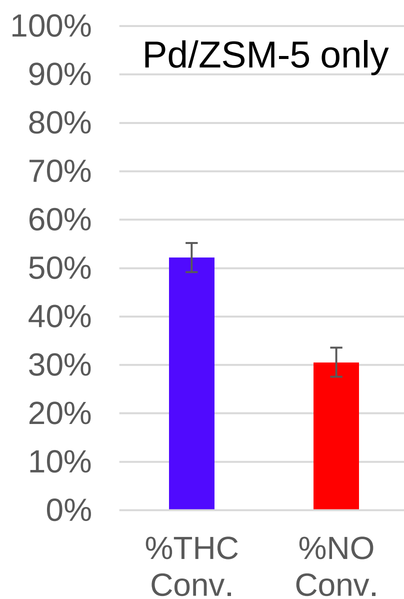
Ramp rate: 40 °C/min

Single HC/NO trap layer

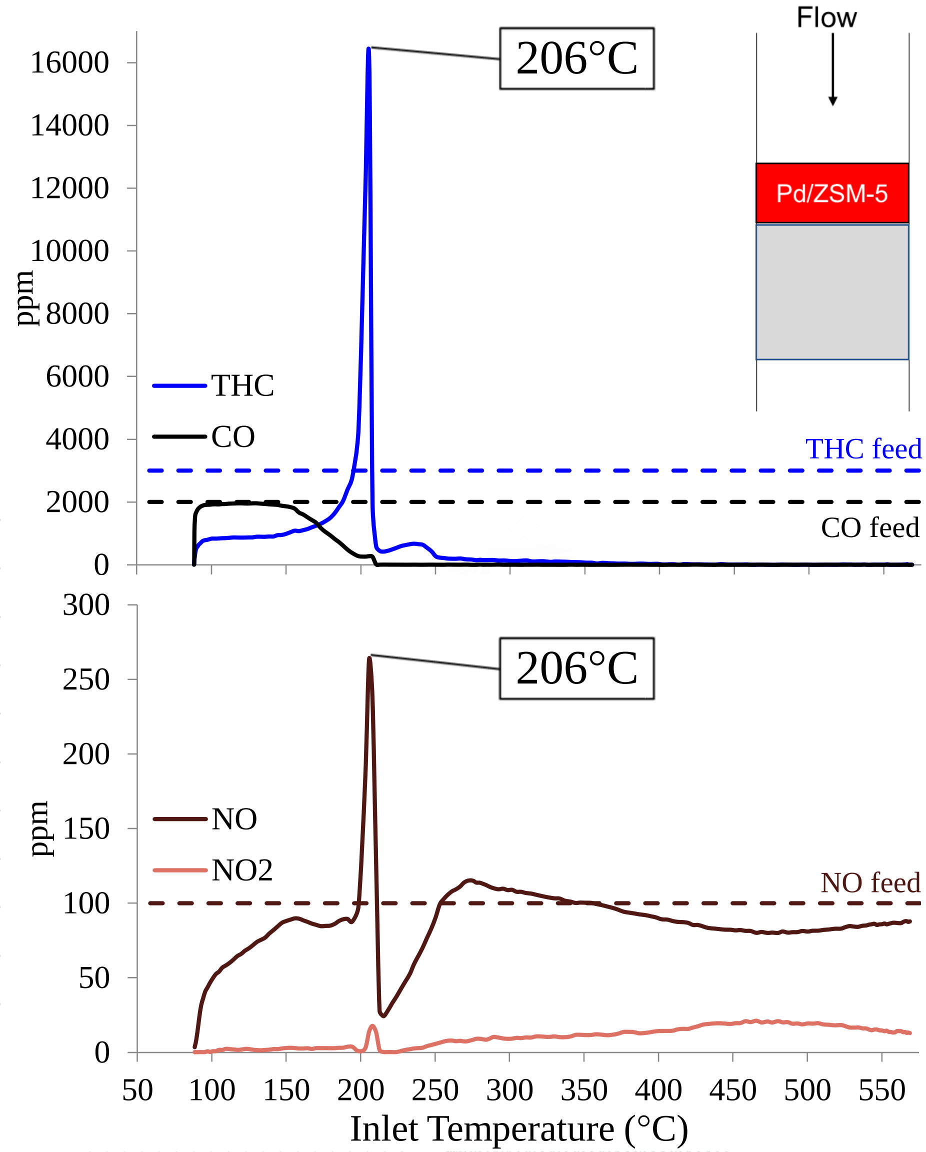
0.2 g 1% Pd/ZSM-5

Total HC_1: 3000 ppm
C_2H_4: 500 ppm
C_3H_6: 300 ppm
C_3H_8: 100 ppm
$C_{10}H_{22}$: 2100 ppm
CO: 2000 ppm
NO: 100 ppm

Also H_2, O_2, H_2O and CO_2



Net conversion quantified between t=0 (~80°C) and 250°C



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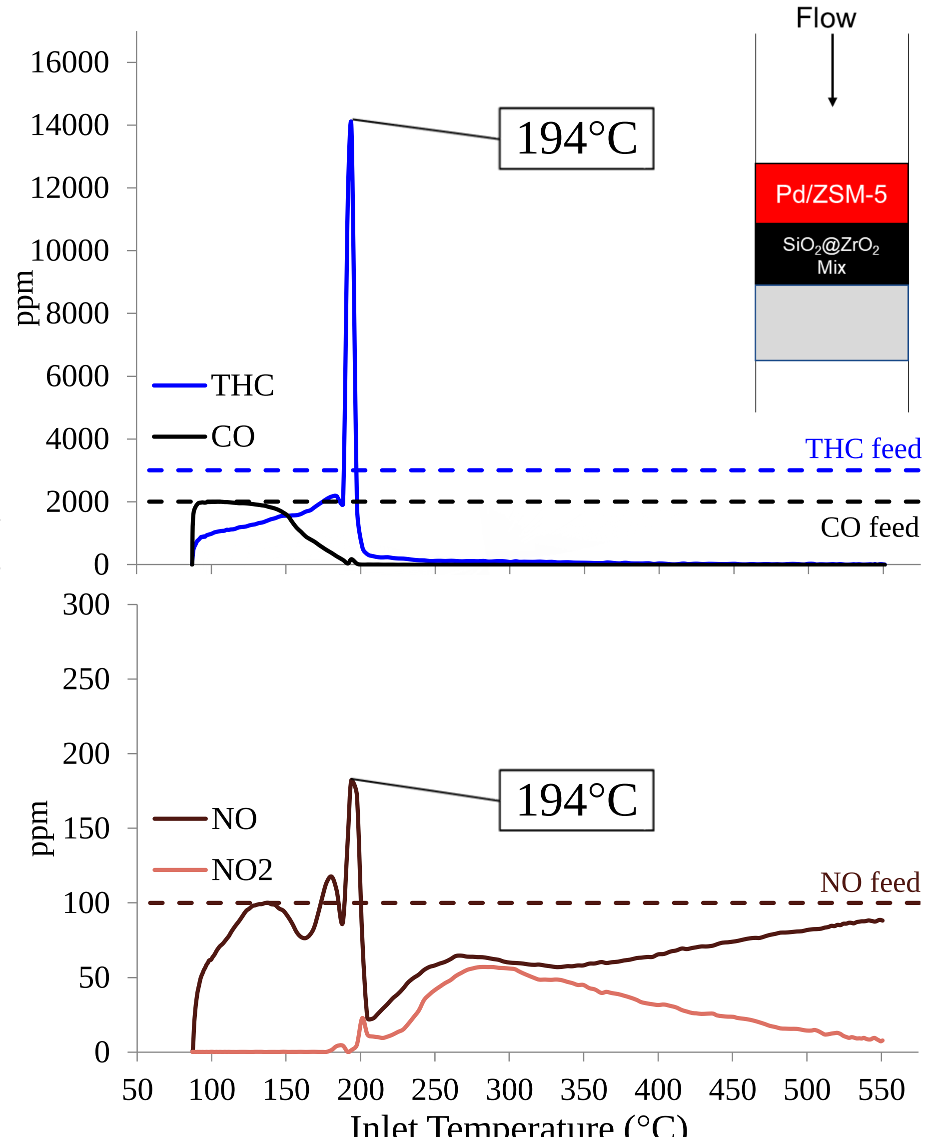
Employing dual-bed configuration leads to decreased peak NO and HC release quantity and temperature

- Peak HC slip and release temperature decreases notably
  - decreases from 206 to 194°C
- With Pt in oxidation catalysts, NO to NO_2 oxidation rate increases
- Indication of HC-SCR apparent between 200 and 250 °C



Ramp rate: 40 °C/min

Dual-bed catalyst layers

0.2 g 1% Pd/ZSM-5

+ 0.1 g 2%$Pd/SiO_2@ZrO_2$

+ 0.1 g 3.6%$Pt/SiO_2@ZrO_2$

Total HC_1: 3000 ppm

C_2H_4: 500 ppm

C_3H_6: 300 ppm

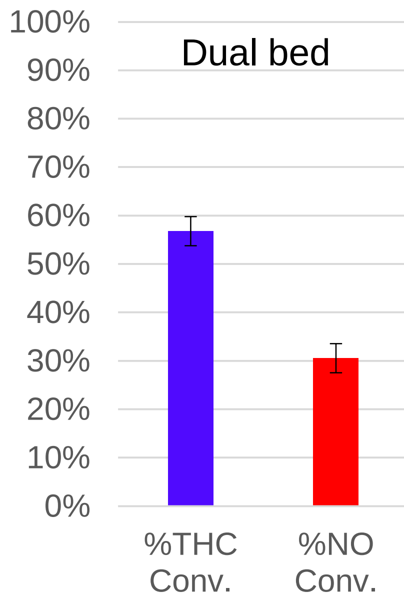
C_3H_8: 100 ppm

$C_{10}H_{22}$: 2100 ppm

CO: 2000 ppm

NO: 100 ppm

Also H_2, O_2, H_2O and CO_2



Net conversion quantified between t=0 (~80°C) and 250°C

Employing mixed-bed configuration drastically decreases peak NO and HC release quantity

- HC slip decreases by 25%
  - quantified between t=0 (~80°C) and 250°C
- Peak release temperature also decreases from 206 to 182-193°C
- Interestingly NO to NO_2 oxidation rate decreases compared to dual-bed
- Indication of HC-SCR still apparent between 200 and 250°C, but less

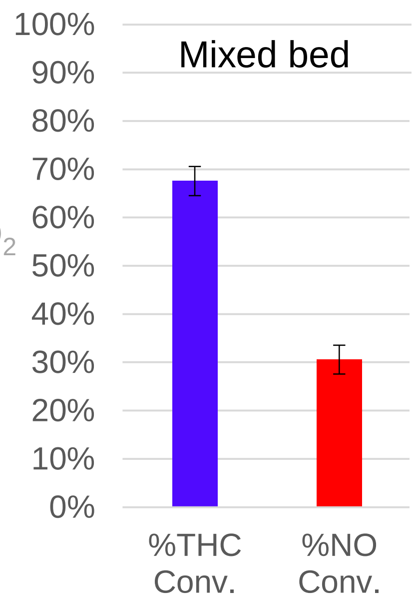
Ramp rate: 40 °C/min

Well-mixed catalyst bed

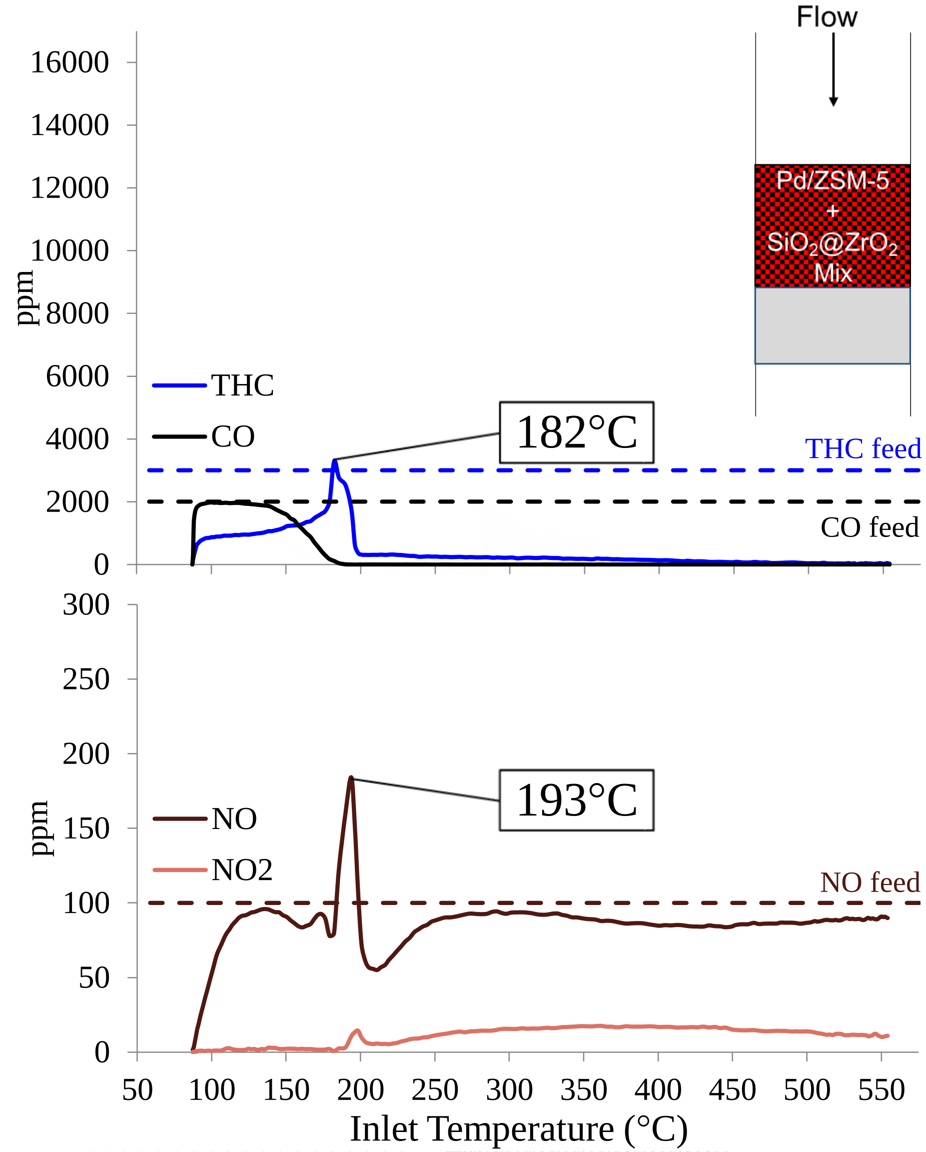
0.2 g 1% Pd/ZSM-5
+ 0.1 g 2% Pd/SiO_2@ZrO_2
+ 0.1 g 3.6% Pt/SiO_2@ZrO_2

Total HC_1: 3000 ppm
C_2H_4: 500 ppm
C_3H_6: 300 ppm
C_3H_8: 100 ppm
$C_{10}H_{22}$: 2100 ppm
CO: 2000 ppm
NO: 100 ppm

Also H_2, O_2, H_2O and CO_2



Net conversion quantified between t=0 (~80°C) and 250°C



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Remaining Challenges

Future Directions

- **Support modifications for enhanced PGM activity**

PGM content should be as small as possible especially for Pt-containing catalysts

Continue to optimize ZrO_2 layer for well-dispersed and stable PGM

Pt-Pd interactions have been shown to have significant advantages, but why is this only observed in physical mixtures here?

Perform extensive bi-metallic materials characterization to better understand PGM state and interactions

USC/Solvay collaboration shows excellent initial activity but needs improved durability

Complete aging study on existing catalysts; introduce metal oxide overlayer

- **Trapping Materials**

Pd/zeolites show excellent effectiveness, but characterization illustrates improved ion-exchanging is necessary

Improve ion-exchange by systematically modifying procedure followed by characterization

ZSM-5 not stable above 750°C, need different zeolite for NO and smaller HCs

Identified supplier of CHA; also targeting new post-doc with zeolite synthesis experience

- **Multifunctional catalyst evaluation**

Need to move to more representative samples with layered washcoats

Continue to improve washcoating technique to allow layered approach

Any proposed future work is subject to change based on funding levels

Responses to 2017 Reviewers (5); overall score = 3.46/4.00

- **Approach (3.6/4.0):**
  - excellent approach to learn fundamentals in applied systems
  - **Checking catalysts with actual exhaust is prudent**
  - **aging impact needs to be addressed more completely**
- **Technical Accomplishments (3.5/4.0):**
  - Advances being made on all fronts
  - **Potential improvements possible with integration**
  - **Make aging criteria more clear**
- **Collaborations (3.1/4.0):**
  - Complex but well-managed project with diverse team
  - **Collaboration will be tested when integrating**
  - **Lack of industry support makes program less valuable in terms of DOE program objective**
- **Future plans (3.4/4.0):**
  - excellent approach to learn fundamentals in applied systems
  - **Would like to see further integration**
  - **Work more actively with industry**
  - **Look at exotherm impact with faster ramp rate**
- **Relevance (100%):**
  - Project will be very critical to low temperature combustion success
  - **Project relevance improved with engine demonstration and vehicle OEM**
- **Resources (60% Insufficient):**
  - **To move into complex layered and multi-component systems with engine testing will not be possible with current budget**

Responsive Actions
1. *Advances in washcoating will allow it* 2. *Aging studies were primary focus this year*
1. *Large focus of this year was in the combined/integrated systems* 2. *Implemented this on slides this year*
1. *No issues to date; catalysts freely move between USC and ORNL* 2. *Knowledge being learned is shared with industry; techniques reported; working with industry*
1. *Primary focus going forward is in multi-finctional systems* 2. *Johnson Matthey collaboration resulted in washcoated samples this year* 3. *Implemented faster ramp in portion of the work this year*
1. *Engine approach is challenging, but a possibility with washcoating*
1. *Although budget decreased this year, request for $500k budget is included for next year*

Summary

- **Relevance:** Develop new emission control technologies to enable fuel-efficient engines with low exhaust temperatures (<150ºC) to meet emission regulations
- **Approach:** employ low temperature protocols to evaluate novel catalysts and systems
- **Collaborations:** Wide-ranging collaboration with industry, academia, & national labs maximizes breadth of study, guides research from other funding sources
- **Technical Accomplishments:**
  - Showed that 10-30% SiO_2 content in Al_2O_3 improves reactivity
  - Demonstrated trap materials function effectively as oxidation catalysts and improve overall performance
  - Verified aging degrades overall trap functionality, but $C_{10}H_{22}$ is still trapped efficiently on the aged sample
  - Demonstrated mixed bed configurations markedly outperform dual bed
  - Washcoated full-size monolith of CCC+Pt/Al_2O_3
  - In collaboration with JMI, washcoated Pd/Ce-Zr_{NP}/Al_2O_3 and Pt/Ce-Zr_{NP}/Al_2O_3 cores
- **Future Work:**
  - Improve ion-exchange in zeolites by systematically modifying procedure followed by characterization; incorporate CHA/SSZ-13 into matrix
  - Continue to optimize ZrO_2 layer for improved surface for well-dispersed and stable PGM
  - Complete aging study on existing catalysts and then explore introduction of optimized metal oxide overlayer

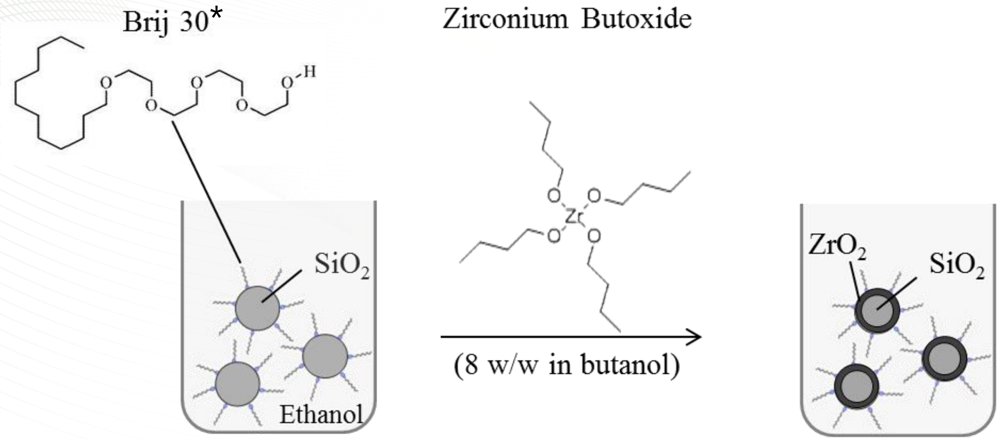
Any proposed future work is subject to change based on funding levels

Technical Backup Slides

USC/Solvay supports

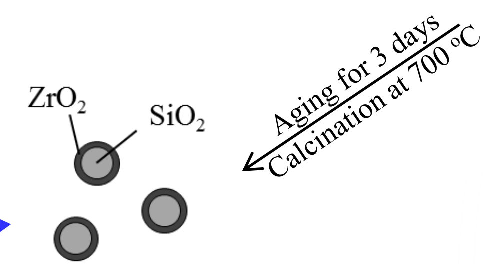
Support	Al (%)	Si (%)	Surf. Area (m^2/g)	PZC (pH)
8	100	0	160	8
2	95	5	105	7.2
3	85	11 + 4% La	171	7.2
5	88	12	249	7.2
6	80	20	292	6.0
1	70	30	160	6.1
A-300 (SiO_2)	0	100	282	3.4

Experiment Detail: Synthesis of SiO_2@ZrO_2 core@shell Oxide Support



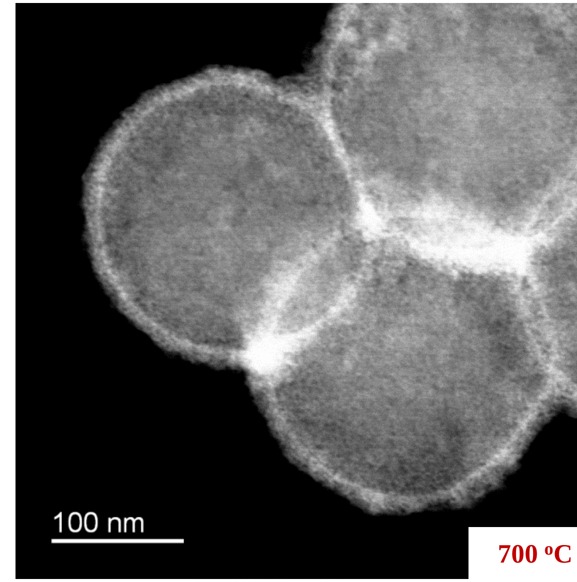
Synthesis of silica spheres

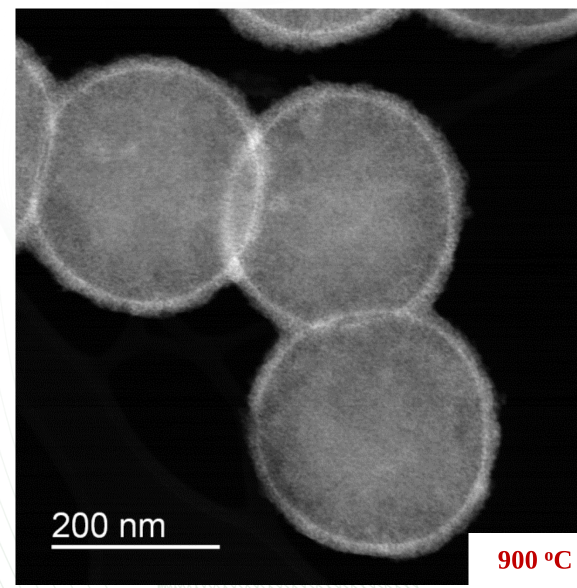
Silica core and amorphous shell with zirconium hydroxide



Material	Surface Area (m^2/g)
ZrO_2	97
ZrO_2-SiO_2	153
SiO_2@ZrO_2	**210**

Silica core and zirconium oxide shell after calcination at 700 ºC





- **SiO_2** is located in the **core** (Si: 14 amu) and **ZrO_2** in the **shell** (Zr: 40 amu).
- The ZrO_2 **shell** seems to be **porous**.
- Growth of SiO_2@ZrO_2 spheres. Shell is maintained. Diameter at: **700 ºC: ~220 nm**
  900 ºC: ~250 nm

*(Brij 30): Polyoxyethylene(4) lauryl ether

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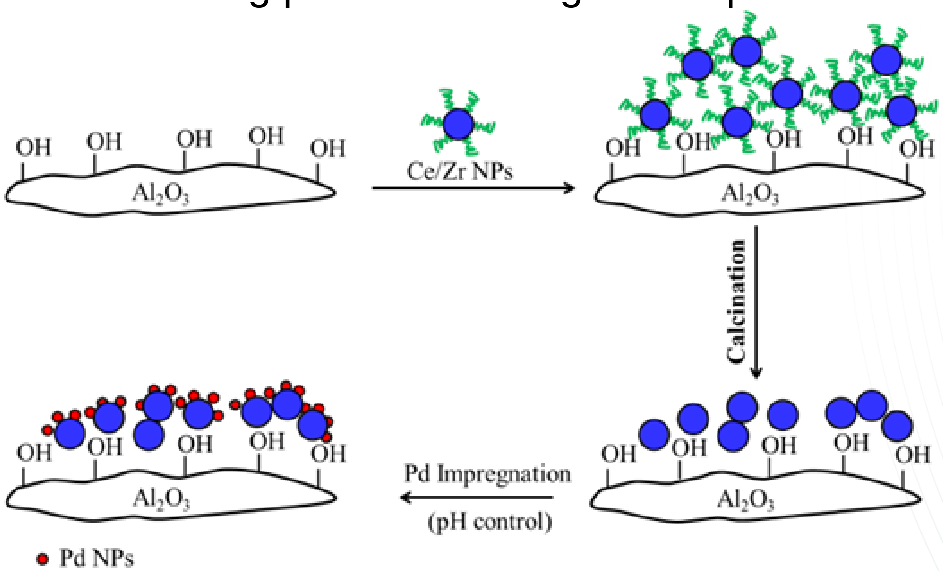
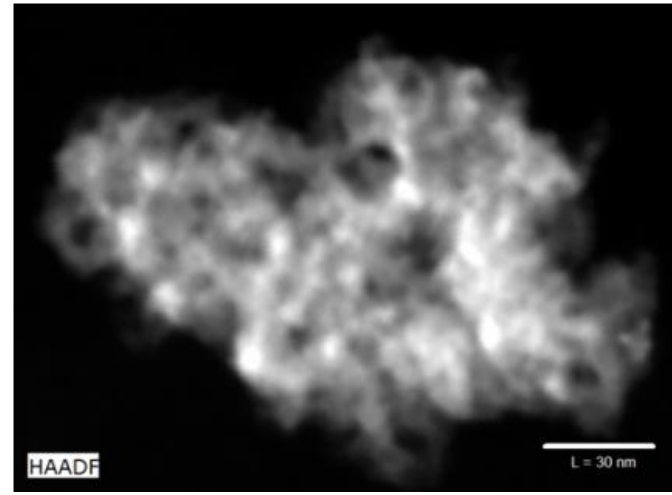
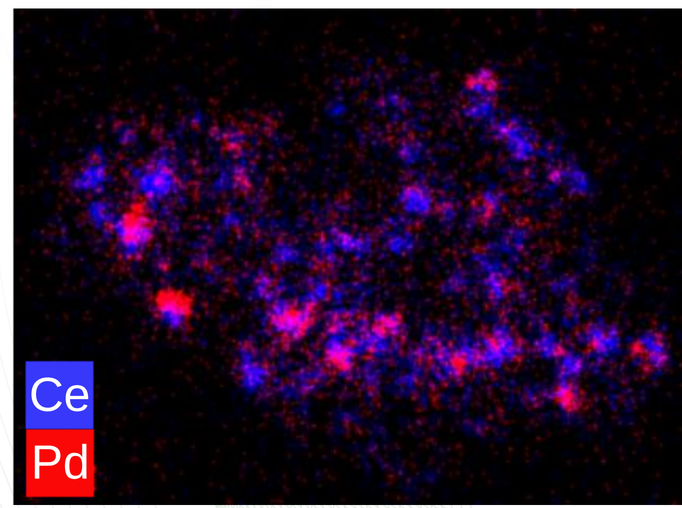
Targeted PGM deposition on nanoparticles of CeO_2 and CeO_2-ZrO_2 to improve durability and activity

- Starting with Ce or CeZr nanoparticles, ~5 nm, and anchor them to high surface area supports
  - In this instance Al_2O_3, but SiO_2 also possible
- Target Pd or Pt deposition on preferred supported metal oxide
  - nano-particles of PGM on nano-particles of Ce-Zr
  - controlling pH enables targeted deposition







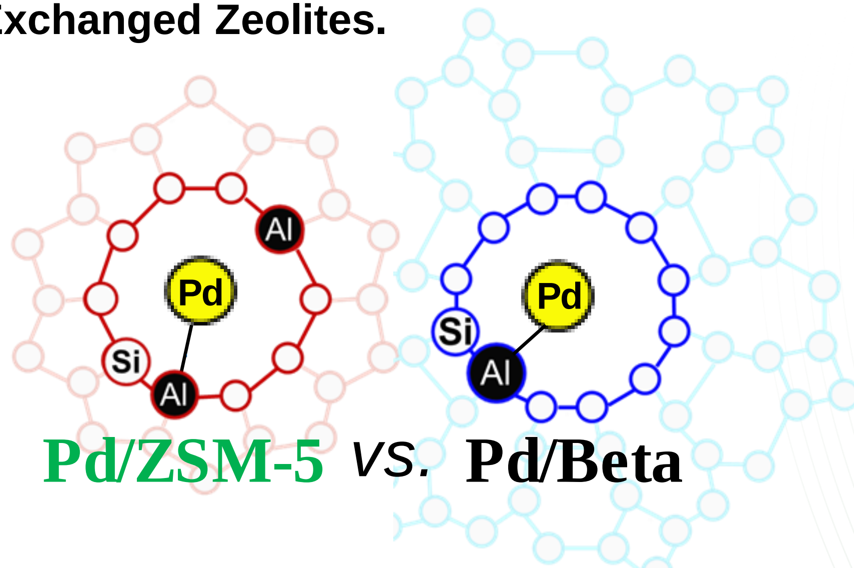
Synthesis of zeolite based HC and NO traps

Strategy

- Understand ZSM-5 and BEA zeolites in HC and NO adsorption and desorption to help optimization.
- Systematic variation of key zeolite properties:
  - **Cation type** (H^+ vs. Ag^+, Pd^{2+})
  - H_2O, CO_2
  - **Pore structure** (BEA vs. ZSM-5)

Zeolite type	Si/Al molar ratio	Nominal cation form	Surface area (m^2/g)
BEA	25	H^+	680
BEA	25	Ag^+/Pd^{2+}	NM
ZSM-5	30	H^+	405
ZSM-5	30	Ag^+/Pd^{2+}	NM

Ion-Exchanged Zeolites.



0, 1, 5 wt.% Ag/BEA
1 wt.% Ag/ZSM-5
1 wt.% Pd/BEA
1 wt.% Pd/ZSM-5

Calcination: 500 ºC (2 h)

Liu, X., Lambert, J.K., Arendarskiia, D.A., Farrauto, R.J., Appl. Catal. B 35 (2001) 125.
Lambert, J.K., Deeba, M., Farrauto, R.J, US Patent 6,074,973 (2000).
Nunan, J., Lupescu, J., Denison, G., Ball, D., Moser, D., SAE Int. J. Fuels Lubr. 6 (2013) 430.